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(54) EXTRUSION OF ETHYLENE POLYMER COMPOSITIONS

(71) We, E.I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the Laws of the State of Delaware, Located at Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

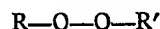
The present invention relates to processes for preparing cross-linkable compositions containing ethylene polymers by continuous extrusion, and to novel cross-linkable compositions containing ethylene polymers.

Batch processes for the preparation of cross-linkable compositions containing ethylene polymers are known and are described in, for example, U.S. Patent Nos. 2,826,570; 2,938,012 and 3,098,831. The ethylene polymer, which is usually in granular form, is charged into a suitable mixing device such as a Banbury mixer or a roll mill with a cross-linking agent such as a suitable peroxide, which is thus incorporated into the polymer. The compounded composition is thereafter chopped into moulding granules, which can be stored until required for use. Shaped articles of cross-linked polymer can be prepared by placing the granules into a suitable mould and then concurrently shaping and cross-linking them by heating the closed mould at an elevated temperature. Alternatively the granules can first be melt-shaped, for example by extrusion as a film, monofilament or wire coating, or by injection moulding and then cross-linked by further heating at higher temperatures. For example, U.S. Patent No. 2,938,012, mentioned above, describes blending polyethylene on a two roll mill with bis (3,4-dichloro- α,α' -dimethylbenzyl) peroxide and thereafter compression moulding the blended composition at 350°F. to give moulded products having a high degree of cross-linking. Batch mixing processes, however, suffer from serious disadvantages, in particular the safety hazards of handling peroxy

compounds in open, batch-type equipment, high cost and inefficiency, and susceptibility to contamination.

It has also been proposed to produce cross-linkable compositions containing ethylene polymers by spray-coating granules of an ethylene polymer with a solution of a peroxide curing agent or by tumbling granules of an ethylene polymer with a powdered solid peroxide curing agent. These techniques do not provide a uniform mixture of the curing agent and the polymer. In consequence, when the cross-linkable compositions so-obtained are melt-shaped into shaped cross-linked compositions, either the product is non-uniform or the cross-linkable composition must, before being shaped, be further mixed while molten, which results in premature cross-linking which makes the shaping operation difficult or impossible.

United States Patent No. 2,528,523 describes the use of certain tertiary peroxides as cross-linking agents for ethylene polymers. The peroxides have the formula



where R and R' are saturated non-aromatic hydrocarbon radicals containing a total of at least eleven carbon atoms and each of the oxygen atoms in the peroxide link is attached to a tertiary carbon atom. This U.S. patent is mainly concerned with the production of cross-linkable compositions by batch mixing of the ethylene polymer and the peroxy compound. However, it does also refer to the possibility, when the polymer is to be extruded, of injecting a liquid peroxy compound, or a solution of a solid peroxy compound in a liquid carrier, into the molten ethylene polymer while the polymer is in the head of the extrusion machine and before it reaches the die. This procedure is stated to be advantageous when a very active peroxide having a high vapour pressure is employed, but no Example of this procedure is given. In a process of this kind the peroxy compound does not become uniformly mixed with polymer, and in conse-

quence the cured product is not uniformly cured.

In its first aspect, the present invention provides a continuous process for producing a cross-linkable composition which comprises:—

- 5 (1) continuously feeding into a screw extruder containing a mixing zone an ethylene polymer (as hereinafter defined);
- 10 (2) continuously converting the ethylene polymer, by the action of the screw extruder, into a homogeneous molten mass having a temperature not higher than 160°C;
- 15 (3) continuously injecting into the said homogeneous molten mass while it is in the mixing zone of the extruder and at a temperature not higher than 160°C, 0.001 to 0.050 part by weight, per part by weight of the ethylene polymer, of a peroxy compound which is dissolved or dispersed in a liquid carrier and which has a flash point of at least 70°C and an equivalent half-life (as hereinafter defined) of more than 1 hour, the said liquid carrier being a light oil or melted wax;
- 20 (4) continuously subjecting the mixture of the peroxy compound, the liquid carrier and the ethylene polymer to the action of the screw extruder, to form a uniform mixture, while maintaining the mixture in the molten state at a temperature not higher than 160°C; and
- 25 (5) continuously extruding the molten mixture from the screw extruder;

35 the average residence time of the peroxy compound in the screw extruder being from 1 to 12 minutes and the conditions being so controlled that the extruded product is substantially free from cross-linking.

40 During the process there may be a very small amount of reaction between the polymer molecules, with a consequent small increase in the average molecular weight of the polymer. However, the conditions of the process must be such that the product is substantially free from cross-linking. Thus any reaction between the polymer molecules during the process must be limited to an amount such that the extrudate, after being chopped into moulding granules, is melt-fabricable by standard techniques, for example those used for melt-shaping cross-linkable ethylene polymer compositions produced by batch-mixing techniques. In this connection it is of interest that the presence of the liquid carrier in the moulding granules provides a compensating factor for any increase in molecular weight of the polymer, so that the Melt Index of the extruded product is usually no greater than that of the starting material (both measured at a temperature at which the peroxy compound is not decomposed, say 115°C).

65 The term "ethylene polymer" as used herein means a polymer which can be cross-linked with the aid of a peroxy compound as defined above and which is a homo-polymer of ethy-

lene, or a copolymer of ethylene with a copolymerisable monomer, said copolymer containing at least 50% by weight of ethylene units, or a blend of a said homopolymer and a said copolymer, or a blend of a said homopolymer and/or a said copolymer with another polymer, which blend contains at least 50% by weight of ethylene units.

70 The ethylene homopolymer can be a high density or low density polyethylene, or a blend of two or more different polyethylenes, for example a blend of high density polyethylene and low density polyethylene. A suitable starting material is a blend of between 50 and 75% by weight of polyethylene having a density of about .921 g/cc and a melt index of about 0.25, the remainder being polyethylene having a density of about .916 g/cc and a melt index of about 12. A preferred polymer is a low density polyethylene of 1.8 melt index and 0.918 g/cc density.

85 The ethylene copolymer can be for example a copolymer of ethylene with vinyl acetate, methacrylic acid or propylene or an ionic copolymer as described in U.S. Patent No. 3,264,272, as well as blends of these copolymers. Blends which are suitable for use as starting materials include low density polyethylene and ethylene/vinyl acetate copolymers, high density polyethylene and ethylene/vinyl acetate copolymers, and other blends of low or high density polyethylene with the copolymers mentioned above.

90 The ethylene polymer starting material generally has a melt index (as determined by the test described in ASTM-D-1238-62 T) of 0.1 to 50, preferably 1 to 4.

95 There can also be fed into the screw extruder with the ethylene polymer one or more other components which do not have any adverse effect on the processing of the ethylene polymer in the screw extruder (and in particular are non-reactive with the peroxy compound added thereto), for example antioxidants, pigments and fillers, e.g. the 2,2,4-trimethyl - 2 - di - hydroquinoline and medium thermal carbon used in the Examples.

100 The invention is illustrated in the accompanying drawings in which the Figure depicts in schematic fashion a screw-extrusion apparatus suitable for carrying out the process of the invention.

105 Referring to the Figure, the ethylene polymer composition is fed from hopper 10 into a feed zone 12 of screw-extruder device 11. The composition is continuously advanced through the extruder device by suitable means such as advancing screw 13. The continuously advancing composition is advanced from feed zone 12 to compression zone 14 wherein the composition is melted. The melt is continuously advanced from compression zone 14 to metering zone 15 and thence to mixing zone 16. In mixing zone 16 the melt is mixed continuously with the solution or dispersion of the 130

peroxy compound, which is added to the melt through injection port 17 which is in communication with mixing zone 16. The mixture is continuously advanced from mixing zone 16 into a discharge zone whence it is extruded through a suitable die member 18 adapted to extrude the composition into any suitable form.

An important feature of the present invention resides in the incorporation into the molten ethylene polymer composition of a peroxy compound which is in the form of a solution or dispersion in a liquid carrier. From 0.001 to 0.050, preferably from 0.01 to 0.02 part by weight, per part by weight of the ethylene polymer of the peroxy compound is added to the melt. Suitable peroxy compounds include those containing two or more peroxy groups, e.g. 2,5 - dimethyl - 2,5 - di(tertiary-butylperoxy)hexyne - 3; 2,5 - dimethyl - 2,5 - di(tertiarybutylperoxy) hexane; α,α' - bis (butylperoxy) diisopropyl benzene; 1,3,5 - tri[2 - (t - butyl - peroxy)isopropyl] - benzene. The peroxy compounds used in the invention must have an equivalent half-life or more than one hour. By this is meant that the peroxy compound is one which, if it is soluble in benzene, has a half-life in benzene (measured as described below) of more than one hour at the extrusion temperature employed, or, if it is not soluble in benzene, so that measurement of its half-life in this way is not possible, has a half-life in the polymer melt which is at least as long as the half-life in the polymer melt of a peroxy compound which has a half-life of more than one hour in benzene at the extrusion temperature employed. Half-life in benzene is discussed fully by Mageli, Bokata and Bolton in publication Reprint No. 30.30 of the Lucidol Division of the Wallace and Tiernan Company (Buffalo, New York). Briefly, the half-life is determined at various temperatures on a peroxy compound having a concentration of 0.2 mol per litre of solution. Aliquots of 10 millilitres each are pipetted into 16 x 150 mm test tubes drawn for rapid sealing. The filled tubes containing about 5 ml. of air space was flushed with dry nitrogen, sealed and heated in a silicone oil bath at a desired temperature for the desired time. Before testing for residual peroxide, the tubes are cooled rapidly in ice water. The test for free peroxide utilises the standard iodometric techniques and involves titration of the liberated iodine with standard sodium thiosulphate solution. Alternatively, infrared differential analysis techniques can be used.

The peroxy compounds used in the invention must also have a flash point of at least 70°C. The flash point of the peroxy compound is measured in accordance with ASTM-D-92-57. Peroxy compounds having a flash point below 70°C. are not suitable because they are too volatile and thus evaporate when added to the polymer melt.

The peroxy compound is dissolved or dispersed, preferably dissolved, in the liquid carrier before it is mixed with the ethylene polymer melt. The liquid carriers used in this invention are light oils, which are preferred, and melted waxes. These carriers do not need to be stripped (i.e. removed) from the resulting extrusion product, either before or after melt-shaping and cross-linking, because the properties of the product are not adversely altered by their presence. Light oils are hydrocarbon fractions from kerosene to mineral oil having a viscosity of between 150 centistokes and 10 centistokes, as measured in accordance with ASTM-D-446. Thus, suitable liquid carriers include mineral oil, mineral spirits and kerosene. The peroxy compound is preferably dissolved in a light oil having a boiling point of at least 200°C., preferably about 250°C. The solution or dispersion of the peroxy compound in the liquid carrier generally contains 35 to 90%, e.g. 35 to 55%, by weight of the peroxy compound, based upon the total weight of the solution or dispersion. When a wax is used as the carrier, any low melting, fatty, plastic, amorphous substance of animal, vegetable, mineral or synthetic origin may be used, the wax usually consists of higher monohydric alcohol esters of fatty acids. "Sunoco" (Registered Trade Mark) Paraffin Wax No. 3425 is a preferred wax of synthetic origin.

An essential feature of the process of the present invention is that the average residence time of the peroxy compound in the extruder is sufficient to ensure uniform mixing but not long enough to produce substantial cross-linking, and is from 1 to 12 minutes, and we believe that at least when using standard extrusion equipment, this means that less than 0.1% of the peroxy compound is retained in the screw extruder for a period longer than four times the said average residence time.

In a typical process, an extruder of either a single or a twin screw construction capable of operating at high rates (2,000 to 10,000 lbs per hour) is run while maintaining a melt temperature which is as low as is consistent with adequate melting of the ethylene polymer. The melt temperature is usually from 110° to 160°C., preferably 130° to 160°C., e.g. 145°C., depending upon the particular ethylene polymer employed.

In its second aspect, the invention provides a solid composition comprising an ethylene polymer (as hereinbefore defined) which is substantially free from cross-linking and which has uniformly distributed therein (a) 0.001 to 0.050 part by weight, per part by weight of ethylene polymer, of a peroxy compound which has a flash point of at least 70°C. and an equivalent half-life (as hereinbefore defined) of more than one hour, and (b) a solvent for the peroxy compound, the peroxy compound constituting 35 to 90% by weight of the total weight of the peroxy compound and the sol-

vent, the solvent being a light oil or a wax.

The invention is illustrated, but not limited by the following Examples, in which all parts and percentages are by weight unless otherwise specified.

The products obtained in the Examples were evaluated in accordance with the following procedures:

10 **TENSILE PROPERTIES** — The tensile properties of cross linked polyethylene sheets, prepared by compression moulding as 6 × 7 inch plaques in a press using a 125-mil chase and 20,000 pounds force at a temperature of 120°C for 5 minutes from the cross-linkable polyethylene produced by the process of this invention and subsequently cured by heating for 15 minutes at 200°C under 20,000 pounds force in a press, were measured in accordance with ASTM-D-08-59 T at a strain rate of 20 inches/minute. Aged tensile tests were obtained from samples aged, after curing, for a period of 6 days at 180°C., one side only being exposed to the atmosphere.

25 **CROSSLINKING** — The degree of cross-linking of the polymer samples was determined both by a "swell test" and an extrusion test conducted as follows:—

30 A round bottom flask with a round glass joint connected to a reflux condenser is used. For a single determination a 500 ml. flask is used. For more than two simultaneous determinations a 2000 ml flask is used. A source of heat sufficient to boil the xylene is supplied.

35 The sample is prepared for testing by wrapping the sample in a pouch of 100 mesh wire cloth prepared by folding a 1 1/2 × 3 inch piece of cloth into a 1 1/2 × 1 1/2 square and taking a 1/4 inch fold on each of the open edges to form a pouch. The edges are then stapled (one side is open). The sample in the pouch is previously ground to 30 mesh sieve size and the fines which pass 60 mesh are rejected and not included in the sample. That which is retained on 60 mesh is put in the pouch and the pouch and sample are weighed. The mesh sizes given herein are U.S. Standard Sieve Sizes.

50 The pouch is then sealed on the fourth side and the sample in the pouch is immersed completely in xylene and suspended in the solution near the bottom of the round bottom flask. About 1% of antioxidant is dissolved in the xylene to prevent further cross-linking of polyethylene. The xylene is boiled vigorously to assure good agitation. Typical boiling rates yield twenty to forty drops/min. from the condenser. The sample is extracted for twelve hours.

60 The sample and pouch are withdrawn from the boiling xylene and immediately placed in a vacuum oven preheated to 150°C. The sample is dried under at least 28 inches of vacuum for 16 hours. The sample is then cooled and weighed.

The percent solvent extraction is calculated as follows.—

$$\% = \frac{W_3 - W_4}{(1-F)(W_2 - W_1)} \times 100$$

where

W_3 = weight of sample in stapled pouch before extraction; 70

W_4 = Weight of sample in stapled pouch after extraction and drying;

F = fraction of xylene insoluble filler in polyethylene; 75

W_2 = weight of sample and pouch with one side open

and W_1 = weight of 100 mesh pouch sealed on three sides. 80

Alternatively the test can be done according to ASTM-D-2765-68-C using xylene. Substantially the same results are achieved.

EXAMPLES 1—6.

Polyethylene compositions as identified in Table I below were extruded on an Egan Extruder No. 22160—2 at a melt temperature of 130°C. and at an extrusion rate of 150 lb/hour. All of the compositions contained 0.5% based on the weight of the ethylene polymer, of "Age-Rite Resin D" which is polymerised 1,2 - dihydro - 2,2,4 - trimethyl-quinoline, an antioxidant sold by Vanderbilt. The compositions used in Examples 1—3 also contained 28.6%, based on the weight of the ethylene polymer, of medium thermal carbon. In each instance a 45% solution of 2,5 - dimethyl - 2,5 - di(tertiarybutylperoxy) hexyne-3 ["Lupersol 130" ("Lupersol" is a Registered Trade Mark) sold by Pennwalt] in mineral oil was injected into the mixing zone of the extruder in amounts as set forth in Table I below. In each instance a cross-linkable polyethylene composition was obtained which was suitable for melt-shaping and cross-linking. 105

The resultant extrudate was chopped into moulding granules. Portions of these were compression moulded at 125°C. for five minutes using 125 mil thick shims to produce plaques 6 × 7 inches in size and about 1/8 inch thick, and the plaques were cured in the press by holding at a temperature of about 200°C. for 15 minutes. Microtensile bars were die-cut from these and tested at a strain rate of 20 inches per minute following ASTM-D-08-59T. The results of these tests are shown in Table II below. The degree of cross-linking was determined as described hereinabove, by extraction using boiling xylene. Another indication of the cross-linking was obtained by the swell test defined in ASTM-D-2765-68-Method. 110

C. In this test a weighed portion of the plaque was immersed in hot xylene at 110°C for 24 hours, removed, blown dry and re- 125

- weighed to determine the weight of xylene swollen polymer. This test is reported as the value of the ratio of the gel volume in swollen polymer divided by original volume of gel in the unswollen state. Thus the smaller the value, the less xylene has been absorbed and hence the greater the cross-linking. This cross-linking is permanent and does not change significantly on aging for six days at 180°C. in an air oven with one surface exposed to the atmosphere, as shown by the data in Table II below for percent extractables which, in every case, decreases slightly on aging, indicating a small increase in degree of cross-linking after six days at 180°C.

TABLE I

Example No	1	2	3	4	5	6
Ethylene Polymer	Alathon 15*	Blend A**	Blend A**	Alathon 15*	Blend A**	Blend A**
Melt Index	4.0	1.25	1.25	4.0	1.25	1.25
Injection rate of Peroxide Solution pounds/hour	5.95	3.57	5.95	8.34	5.0	8.34
% of Peroxy Compound by weight based upon total weight of polyethylene	2.5	1.5	2.5	2.5	1.5	2.5
% of Mineral oil, by weight based upon total weight of polyethylene	3.1	1.8	3.1	3.1	1.8	3.1
% of medium thermal carbon by weight based upon total weight of polyethylene	28.6	28.6	28.6	None	None	None

* "Alathon" is the Du Pont trademark for branched polyethylene resin of melt index 4 and density of 0.917 g/cc

** Blend A is a blend of 60% by weight branched polyethylene of 0.25 melt index and 0.921 g/cc density and 40% by weight branched polyethylene of 12 melt index and 0.916 g/cc density.

TABLE II

Physical Properties of Crosslinked Polyethylene Products

Example No.	1	2	3	4	5	6
Xylene Extraction:						
Orig Swell	6.2	5.2	4.0	5.0	9.7	5.3
Orig. % Extr	14.3	9.5	9.1	8.4	11.4	8.9
Aged Swell	5.2	5.3	4.1	4.2	6.2	4.3
Aged % Extr.	10.2	9.3	6.6	6.2	10.8	6.7
Room Temperature Tensiles:						
Orig. Yield, psi	1146	1362	1079	850	1260	950
Orig. Break, psi	2402	2768	2879	1320	2520	1480
Orig. % Elong.	284	334	276	300	540	260
Aged Yield, psi	1160	1354	1215	970	1350	980
Aged Break, psi	1556	2457	2145	2000	2680	1480
Aged % Elong.	135	205	182	380	640	180

WHAT WE CLAIM IS:—

1. A continuous process for producing a cross-linkable composition which comprises:—
 - (1) continuously feeding into a screw extruder containing a mixing zone an ethylene polymer (as hereinbefore defined);
 - (2) continuously converting the ethylene polymer, by the action of the screw extruder, into a homogeneous molten mass having a temperature not higher than 160°C;
 - (3) continuously injecting into the said homogeneous molten mass while it is in the mixing zone of the extruder and at a temperature not higher than 160°C, 0.001 to 0.050 part by weight, per part by weight of the ethylene polymer, of a peroxy compound which is dissolved or dispersed in a liquid carrier and which has a flash point of at least 70°C. and an equivalent half-life (as hereinbefore defined) of more than 1 hour, the said liquid carrier being a light oil or a melted wax;
 - (4) continuously subjecting the mixture of the peroxy compound, the liquid carrier and the ethylene polymer to the action of the mixing section of the screw extruder, to form a uniform mixture, while maintaining the mixture in the molten state at a temperature not higher than 160°C; and
 - (5) continuously extruding the molten mixture from the screw extruder;
- the average residence time of the peroxy compound in the screw extruder being from 1 to 12 minutes and the conditions being so controlled that the extruded product is substantially free from cross-linking.
2. A process according to claim 1 wherein in step (3) there is injected into the homogeneous molten mass a solution or dispersion of the peroxy compound in the liquid carrier, the solution or dispersion containing 35 to 90% by weight of the peroxy compound, based on the weight of the solution or dispersion.
 3. A process according to claim 1 or 2 wherein the liquid carrier is a light oil (as hereinbefore defined) having a boiling point of at least 200°C.
 4. A process according to claim 3 wherein the light oil has a boiling point of about 250°C.
 5. A process according to claim 3 or 4 wherein the light oil is selected from mineral oil, mineral spirits and kerosene.
 6. A process according to claim 1 or 2 wherein the liquid carrier is a melted wax.
 7. A process according to any one of the preceding claims wherein the peroxy compound

is 2,5 - dimethyl - 2,5 - di(tertiary butylperoxy)hexyne-3.

8. A process according to any one of claims 1 to 6 wherein the peroxy compound is 2,5-dimethyl - 2,5 - di(tertiarybutylperoxy)hexane, α, α' - bis(butylperoxy)diisopropyl benzene, or 1,3,5 - tri[2 - tertiarybutylperoxy]isopropylbenzene.

9. A process according to any one of the preceding claims wherein the amount of the peroxy compound added to the homogeneous molten mass is 0.01 to 0.02 part by weight per part by weight of the ethylene polymer.

10. A process according to any one of the preceding claims wherein the ethylene polymer has a melt index (measured as described herein) of 1 to 4.

11. A process according to claim 10 wherein the ethylene polymer is polyethylene.

12. A process according to claim 11 wherein the ethylene polymer is a blend of high density polyethylene and low density polyethylene.

13. A process according to claim 11 wherein the ethylene polymer is a blend of 50 to 75% by weight of polyethylene having a density of about 0.921 g/cc and a melt index of about 0.25 and 50 to 25% by weight of polyethylene having a density of about 0.916 g/cc and a melt index of about 12.

14. A process according to claim 11 wherein the ethylene polymer is polyethylene having a density of 0.918 g/cc and a melt index of 1.8.

15. A process according to any one of claims 1 to 10 wherein the ethylene polymer is a copolymer of ethylene and a copolymerisable monomer or a blend of polyethylene and another polymer.

16. A process according to any one of the preceding claims wherein there is also fed into the screw extruder with the ethylene polymer one or more other components which do not have any adverse effect on the processing of the ethylene polymer in the screw extruder.

17. A process according to any one of the preceding claims wherein the homogeneous molten mass has a temperature of 110° to 160°C., and the mixture of the peroxy compound, liquid carrier and ethylene polymer is maintained at a temperature of 110 to 160°C.

18. A process according to claim 17 wherein the said temperatures are from 130° to 160°C.

19. A process according to any one of the preceding claims wherein less than 0.1% of the peroxy compound is retained in the screw extruder for a time more than four times the said average residence time.

20. A process according to claim 1 substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

21. A process according to claim 1 substan-

tially as described in any one of the foregoing Examples.

22. An extruded cross-linkable composition produced by a process as claimed in any one of claims 1 to 18.

23. An extruded cross-linkable composition produced by a process as claimed in claim 19.

24. A cross-linked composition obtained by heating a composition as claimed in claim 22.

25. A cross-linked composition obtained by heating a composition as claimed in claim 23.

26. A solid composition comprising an ethylene polymer (as hereinbefore defined) which is substantially free from cross-linking and which has uniformly distributed therein (a) 0.001 to 0.050 part by weight, per part by weight of ethylene polymer, of a peroxy compound which has a flash point of at least 70°C and an equivalent half-life (as hereinbefore defined) of more than 1- hour, and (b) a solvent for the peroxy compound, the peroxy compound constituting 35 to 90% by weight of the total weight of the peroxy compound and the solvent, the solvent being a light oil or a wax.

27. A composition according to claim 26 wherein the solvent is a light oil as defined in any one of claims 3 to 5.

28. A composition according to claim 26 or 27 wherein the peroxy compound is 2,5-dimethyl - 2,5 - di(tertiarybutylperoxy) hexyne-3.

29. A composition according to claim 26 or 27 wherein the peroxy compound is 2,5 - dimethyl - 2,5 - di(tertiarybutylperoxy) hexane, α, α' - bis(butylperoxy) diisopropyl benzene, or 1,3,5 - tri - [2 - (tertiarybutylperoxy) isopropyl] - benzene.

30. A composition according to any one of claims 26 to 29 which contains 0.01 to 0.02 part by weight of the peroxy compound per part by weight of the ethylene polymer.

31. A composition according to any one of claims 26 to 30 wherein the ethylene polymer is an ethylene polymer as defined in any one of claims 10 to 15.

32. A cross-linked composition obtained by heating a composition as claimed in any one of claims 26 to 31.

33. A continuous process for producing a cross-linkable composition which comprises:

(1) continuously feeding into a screw extruder containing a mixing zone an ethylene polymer which has a melt index of 1 to 4 and which is a high density polyethylene, a low density polyethylene, or a mixture of high and low density polyethylenes;

(2) continuously converting the polymer by the action of the screw extruder into a homogeneous molten mass having a temperature not higher than 160°C;

(3) continuously injecting into the said homogeneous molten mass while it is in the mixing zone of the extruder and at a

- temperature not higher than 160°C.; 0.01 to 0.02 part by weight, per part by weight of the polymer, of a peroxy compound selected from 2,5 - dimethyl - 2,5 - di(tertiarybutylperoxy)hexyne-3; 2,5 - dimethyl - 2,5 - di(tertiarybutylperoxy)hexane; α,α' - bis(butylperoxy)diisopropyl benzene and 1,3,5 - tri[2 - (t - butylperoxy)isopropyl] benzene, which peroxy compound is dissolved in mineral oil to form a solution containing 35 to 90% by weight of the peroxy compound;
- (4) continuously subjecting the mixture of the peroxy compound, mineral oil and polymer to the action of the mixing section of the screw extruder, to form a uniform mixture, while maintaining the mixture in the molten state at a temperature no higher than 160°C; and
- (5) continuously extruding the molten mixture from the screw extruder;
- the average residence time of the peroxy compound in the screw extruder being from 1 to 12 minutes and the conditions being so controlled that the extruded product is substantially free from cross-linking.
34. A process according to claim 33 wherein

the said temperature is from 130° to 160°C.

35. A cross-linkable composition produced by a process as claimed in claim 33 or 34.

36. A solid composition comprising a polymer which is substantially free from cross-linking, which is a high density polyethylene, a low density polyethylene or a mixture of high and low density polyethylenes, and which has uniformly distributed therein (a) 0.01 to 0.02 part by weight, per part by weight of the polymer, of a peroxy compound selected from 2,5-dimethyl - 2,5 - di(tertiarybutylperoxy)hexyne-3, 2,5 - dimethyl - 2,5 - di(tertiarybutylperoxy) - hexane; α,α' - bis(butylperoxy) diisopropyl benzene and 1,3,5 - tri[2 - t - butylperoxy]isopropyl] benzene, and (b) a mineral oil, the peroxy compound constituting 35 to 90% by weight of the total weight of the peroxy compound and mineral oil.

37. A cross-linked composition obtained by heating above 160°C a composition as claimed in claim 35 or 36.

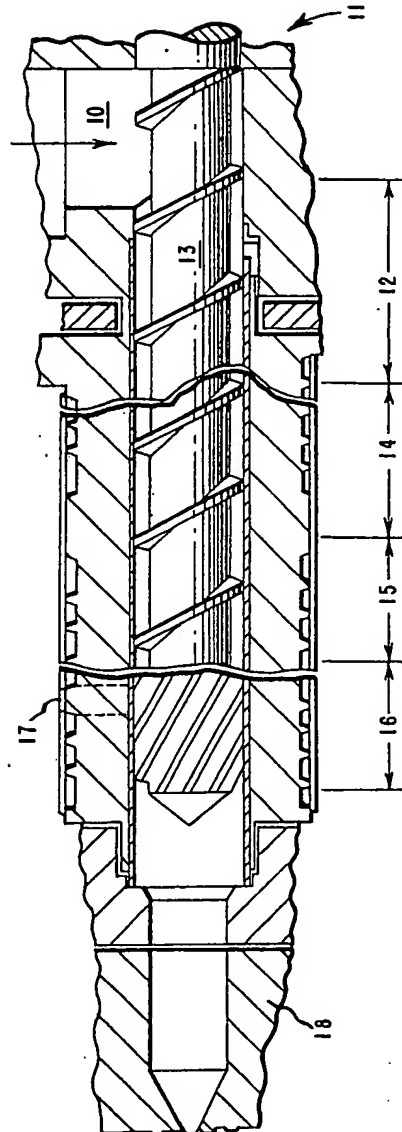
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